

Superconductivity versus structural phase transition in the closely related $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ and $\text{Bi}_2\text{Rh}_3\text{S}_2$

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Single crystals of $\text{Bi}_2\text{Rh}_3\text{S}_2$ and $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ were synthesized by solution growth and the crystal structures, thermodynamic and transport properties of both compounds were studied. In the case of $\text{Bi}_2\text{Rh}_3\text{S}_2$, a structural first-order transition at around 165 K is identified by single crystal diffraction experiments, with clear signatures visible in resistivity, magnetization and specific heat data. No superconducting transition for $\text{Bi}_2\text{Rh}_3\text{S}_2$ was observed down to 0.5 K. In contrast, no structural phase transition at high temperature was observed for $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$, however bulk superconductivity with a critical temperature, $T_c \approx 1.7$ K was observed. The Sommerfeld coefficient γ and the Debye temperature (Θ_D) were found to be $9.41 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and 209 K respectively for $\text{Bi}_2\text{Rh}_3\text{S}_2$, and $22 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and 196 K respectively for $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$. Study of the specific heat in the superconducting state of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ suggests that $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ is a weakly coupled, BCS superconductor.

I. INTRODUCTION

Superconductivity and charge density waves (CDWs) are fascinating and closely linked collective phenomena. The CDW in low dimensional materials was first proposed by Peierls^{1,2}, who showed that a one dimensional metal was unstable against a periodic lattice distortion which creates an energy gap at the Fermi level. Superconductivity and CDW states were linked when Fröhlich proposed a mechanism of superconductivity based on a sliding, incommensurate CDW³. Following the formulation of the BCS theory⁴ of superconductivity, it was appreciated that the superconducting state and the CDW state are both results of electron-phonon coupling often with the CDW state competing with and ultimately replacing the superconducting state as electron-phonon coupling is increased. In some, relatively rare, compounds both transitions can be found upon cooling; more often, though, a CDW or some other type of structural phase transition removes density of states at the Fermi surface and thus suppresses or even precludes the formation of a superconducting state.

It is interesting to study the properties of the materials which manifest the co-existence of superconducting and CDW states, so as to gain a better understanding of how they compete with each other for the density of states as each opens a gap at the Fermi level^{5–15}. The electrical transport properties of some ternary, metal-rich chalcogenides^{16–18}, $\text{A}_2\text{M}_3\text{X}_2$ ($\text{A}=\text{Sn}, \text{Pb}, \text{In}, \text{Tl}$ and Bi ; $\text{M}=\text{Co}, \text{Ni}, \text{Rh}$ and Pd ; $\text{X}=\text{S}$ and Se) have been reported by Natarajan and co-workers¹⁹ with some members of this family showing superconductivity at low temperature^{20–22}. Recently Sakamoto and co-workers reported that parkerite-type $\text{Bi}_2\text{Rh}_3\text{Se}_2$ ²³ was a new superconducting compound (with a critical temperature, $T_c \sim 0.7$ K) with a possible higher temperature CDW transition at $T_{CDW} \approx 250$ K. Pressure studies on this compound²⁴ found that the resistivity anomaly at 250 K

shifted to higher temperature with increasing pressure, which is unusual for a conventional CDW transition^{25–27}. Given that isostructural $\text{Bi}_2\text{Rh}_3\text{S}_2$ is reported to have a resistive anomaly near 160 K (having been measured down to 77 K)¹⁹, measurements of single crystalline $\text{Bi}_2\text{Rh}_3\text{S}_2$ to lower temperatures are called for.

Using solution growth out of a Rh rich Rh-Bi-S melt²², our initial growth attempts produced large grain, crystalline material that showed a clear resistivity feature near 160 K but also an apparent superconducting transition near 2 K. These results indicated that there may be some form of competition or interaction between structural phase transition and superconductivity in this ternary system. A powder x-ray diffraction measurement revealed the anticipated $\text{Bi}_2\text{Rh}_3\text{S}_2$ phase, but also indicated the presence of a second phase.

In order to better understand the physics and chemistry of this part of the Bi-Rh-S system, in this paper we present details of the crystal growth of both $\text{Bi}_2\text{Rh}_3\text{S}_2$ and a new phase: $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$, provide structural data, and present and analyze thermodynamic and transport data from each compound. Whereas $\text{Bi}_2\text{Rh}_3\text{S}_2$ manifests a first order, structural phase transition near 160 K and does not superconduct for $T > 0.5$ K, $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ manifests no signs of any phase transition for $2 \text{ K} < T < 300 \text{ K}$ has a significantly larger electronic specific heat coefficient, γ , and manifests bulk superconductivity below 2 K. Instead of finding the co-existence of a structural phase transition and subsequent superconductivity in one compound we found two closely related compounds: one that manifests a structural phase transition near 160 K and has a relatively lower electronic specific heat at low temperatures and another that does not undergo a structural phase transition upon cooling, has a relatively larger electronic specific heat and does become superconducting below 2 K.

II. EXPERIMENTAL METHODS

Single crystals of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ and $\text{Bi}_2\text{Rh}_3\text{S}_2$ were produced using solution growth techniques^{22,28,29}. For $\text{Bi}_2\text{Rh}_3\text{S}_2$, a mixture of elemental Rh, Bi and S was placed in a 2 mL fritted alumina crucible³⁰ with a molar ratio of Rh:Bi:S = 42.6:28.2:29.2 and sealed in a silica ampule under partial pressure of high purity argon gas. The sealed ampule was heated to 1150°C over 12 hours and held there for 3 hours. After that, it was cooled to 900°C over 70 hours and excess liquid was decanted using a centrifuge. For $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$, a molar ratio of Rh:Bi:S = 55:22.5:22.5 was used, heated and cooled in a similar manner but slowly cooled to 775°C before decanting.

Powder X-ray diffraction data were collected by using a Rigaku Miniflex II diffractometer at room temperature (Cu K_α radiation). Samples were prepared by grinding single crystals into powder and spreading them onto a thin grease layer coated single crystal Si, low background puck. Powder x-ray diffraction data were analyzed using GSAS^{31,32} program.

Single crystal diffraction data were measured using a Bruker Smart Apex CCD diffractometer³³ with Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$). Data were collected with mixed ω/ϕ scan modes and with an exposure time of 10 s per frame. The 2θ range covered from 6° to 64°. Intensities were extracted and corrected for Lorentz and polarization effects with the SAINT program. Empirical absorption corrections³⁴ were accomplished with SADABS, which is based on modeling a transmission surface by spherical harmonics employing equivalent reflections with $I > 3\sigma(I)$. Using the SHELXTL package³⁵, crystal structures were solved using direct methods and refined by full-matrix least-squares on F^2 . Lattice parameters were refined using single crystal diffraction data and are summarized in Table I. Atomic coordinates and displacement parameters with fully site occupation for $\text{Bi}_2\text{Rh}_3\text{S}_2$ and $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ are given in Table II.

The ac resistivity ($f = 17 \text{ Hz}$) was measured as a function of temperature by the standard four probe method in a Quantum Design, Physical Property Measurement System (PPMS) instrument. Depending on the sample size Pt or Au wires (with the diameter of 25 μm or 12.7 μm respectively) were attached to the samples using Epotek-H20E silver epoxy or DuPont 4929N silver paint. The specic heat was measured by using the relaxation method in a Physical Property Measurement System. The ^3He option was used to obtain a measurements down to 0.4 K. The DC magnetization measurements were performed in a Quantum Design, Magnetic Property Measurement System (MPMS).

TABLE I. Lattice parameters of $\text{Bi}_2\text{Rh}_3\text{S}_2$ (293 K and 120 K) and $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ at 293 K. All values are from single crystal diffraction data.

Formula	$\text{Bi}_2\text{Rh}_3\text{S}_2$ (293 K)	$\text{Bi}_2\text{Rh}_3\text{S}_2$ (120 K)	$\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ (293 K)
Formula weight	790.81	790.81	842.27
Z-formula units	4	12	4
Space group	C2/m	C2/m	C2/m
a (Å)	11.291(3)	11.542(2)	11.5212(3)
b (Å)	8.378(2)	8.341(2)	7.9408(2)
c (Å)	7.942(4)	17.768(4)	7.8730(3)
β	133.286(2)°	107.614(2)°	128.033(2)°
Volume (Å ³)	546.8(3)	1630.4(5)	567.33(3)
Density (g/cm ³)	9.605	9.664	9.861

III. RESULTS

A. Phases and structures

The room temperature powder X-ray diffraction pattern from ground, phase pure, single crystals of $\text{Bi}_2\text{Rh}_3\text{S}_2$ are shown in Fig. 1. Single crystal x-ray diffraction used to refine the lattice parameter of $\text{Bi}_2\text{Rh}_3\text{S}_2$ with monoclinic C2/m symmetry, $a = 11.291(3) \text{ \AA}$, $b = 8.378(2) \text{ \AA}$, $c = 7.942(4) \text{ \AA}$, and $\beta = 133.286(2)^\circ$. These crystallographic parameters are within three standard deviations from literature data of $\text{Bi}_2\text{Rh}_3\text{S}_2$ ^{19,36}. Also these lattice parameters were used to fit the powder x-ray diffraction data shown in Fig. 1. Resistivity data measured on $\text{Bi}_2\text{Rh}_3\text{S}_2$ single crystals show only a single transition at $\sim 165 \text{ K}$ (see Fig. 6 below), with no superconductivity being observed down to 0.5 K.

To understand the phase transition of $\text{Bi}_2\text{Rh}_3\text{S}_2$ at 165 K, a set of single crystal X-ray diffraction intensity data of $\text{Bi}_2\text{Rh}_3\text{S}_2$ was collected at low-temperature (LT), ca. 120 K. As shown in Fig. 2, extra diffraction spots, not belonging to the unit cell of $\text{Bi}_2\text{Rh}_3\text{S}_2$ at room-temperature ($a = 11.291(3) \text{ \AA}$, $b = 8.378(2) \text{ \AA}$, $c = 7.943(4) \text{ \AA}$, $\beta = 133.286(2)^\circ$), were observed in the (h0l) zone prerecession image. However, all spots could be completely indexed by a larger monoclinic unit cell (C2/m, $a = 11.542(2) \text{ \AA}$, $b = 8.341(2) \text{ \AA}$, $c = 17.768(4) \text{ \AA}$, $\beta = 107.614(2)^\circ$), which is about 3 times larger than the unit cell at room-temperature (RT), cf. Table I. Comparison of the RT and LT structures of $\text{Bi}_2\text{Rh}_3\text{S}_2$, shown in Fig. 3, indicate that the flat two-dimensional (2D) layers in the RT structure (parallel to ab-plane) are periodically puckered in the LT superstructure.

The x-ray powder diffraction pattern of a ground, phase pure, single crystal of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ is shown in Fig. 4. According to single crystal X-ray diffraction analyses (Table I), $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ also crystallizes in monoclinic symmetry C2/m ($a = 11.5212(3) \text{ \AA}$, $b = 7.9408(2) \text{ \AA}$, $c = 7.8730(3) \text{ \AA}$, and $\beta = 128.033(2)^\circ$). These lattice parameters were used to fit the powder x-ray diffraction

TABLE II. Atomic coordinates and equivalent isotropic displacement parameters of $\text{Bi}_2\text{Rh}_3\text{S}_2$ (293 K and 120 K) and $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$. All the sites are fully occupied. (U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.)

Atom	Wyck	Symm.	x	y	z	$U_{eq} \text{\AA}^2$
$\text{Bi}_2\text{Rh}_3\text{S}_2$ (293 K)						
Bi1	4i	m	0.0002(1)	0	0.2518(2)	0.009(1)
Bi2	4i	m	0.5086(1)	0	0.2596(2)	0.012(1)
Rh1	4f	-1	0.25	0.25	0.5	0.009(1)
Rh2	4i	m	0.2472(1)	0	0.2472(2)	0.015(1)
Rh3	4h	2	0	0.2411(2)	0.5	0.013(1)
S	8j	1	0.2235(6)	0.2704(5)	0.187(1)	0.010(1)
$\text{Bi}_2\text{Rh}_3\text{S}_2$ (120 K)						
Bi1	4i	m	0.0709(1)	0	0.4167(1)	0.017(1)
Bi2	4i	m	0.2432(1)	0	0.2599(1)	0.018(1)
Bi3	4i	m	0.4026(1)	0	0.0830(1)	0.018(1)
Bi4	4i	m	0.5778(1)	0	0.4148(1)	0.017(1)
Bi5	4i	m	0.7383(1)	0	0.2464(1)	0.018(1)
Bi6	4i	m	0.9041(1)	0	0.0831(1)	0.018(1)
Rh1	8j	1	0.3196(2)	0.2470(3)	0.1674(1)	0.018(1)
Rh2	8j	1	0.4092(2)	0.2517(3)	0.3347(1)	0.017(1)
Rh3	4i	m	0.1550(3)	0	0.0983(2)	0.019(1)
Rh4	4i	m	0.1802(3)	0	0.5923(2)	0.019(1)
Rh5	4i	m	0.4860(3)	0	0.2499(2)	0.017(1)
Rh6	4h	2	0	0.2670(5)	0.5	0.018(1)
Rh7	4e	-1	0.25	0.25	0	0.018(1)
S1	8j	1	0.0187(6)	0.2265(10)	0.2464(4)	0.018(1)
S2	8j	1	0.1262(6)	0.2706(10)	0.0806(4)	0.019(1)
S3	8j	1	0.3000(6)	0.2299(9)	0.4232(4)	0.016(1)
$\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$						(293 K)
Bi1	4i	m	0.1896(1)	0	0.1932(1)	0.009(1)
Bi2	4i	m	0.2525(1)	0	0.7483(1)	0.008(1)
Rh1	4i	m	0.0200(1)	0	0.3371(2)	0.008(1)
Rh2	2d	2/m	0	0.5	0.5	0.007(1)
Rh3	4g	2	0	-0.3114(1)	0	0.008(1)
Rh4	4e	-1	0.25	0.25	0	0.013(1)
S	8j	1	-0.0031(3)	-0.2889(3)	0.2908(4)	0.008(1)

data shown in Fig. 4. Fig. 5 shows the structure of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ viewed along the (010) direction. Compared to the RT structure of $\text{Bi}_2\text{Rh}_3\text{S}_2$, Fig. 3(a), the 2D layers in $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ are extensively puckered or distorted in response to the insertion of additional Rh atoms into octahedral vacancies between adjacent layers. As will be discussed below, the low temperature electronic specific heat of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ is almost double that of $\text{Bi}_2\text{Rh}_3\text{S}_2$, consist with superconductivity in the former but not the latter.

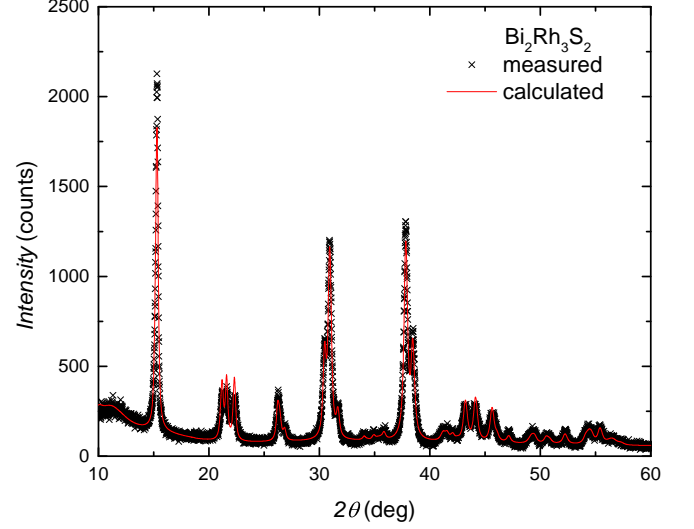


FIG. 1. Powder diffraction pattern of pure $\text{Bi}_2\text{Rh}_3\text{S}_2$. The red line represents the calculated diffraction pattern

B. Physical properties of $\text{Bi}_2\text{Rh}_3\text{S}_2$

The temperature dependent electrical resistivity data from $\text{Bi}_2\text{Rh}_3\text{S}_2$ (Fig. 6) show a sharp feature associated with a 165 K transition with no superconducting transition observed down to 0.5 K. This material shows clear in-plane anisotropy in resistivity. Fig. 6 presents the data from two samples with current flowing along each of the edge directions indicated in the lower inset. The residual resistivity ratio (RRR) values are found to be 53 and 15 in these two directions suggesting that the in-plane scattering and/or the Fermi velocity is anisotropic. Above 170 K the resistivity increases monotonically with temperature, showing metallic behavior. Around 165 K a sudden increase or decrease of resistivity with decreasing temperature is observed in the two different, in-plane, current directions. Below 160 K, resistivity again shows metallic like behavior down to 0.5 K. The upper inset to Fig. 6 shows a 2-5 K thermal hysteresis observed in the resistivity jump near 165 K, suggesting a first-order phase transition, as confirmed by our single crystal X-ray diffraction analyses. Whereas this behavior is typical for structural transition, it is less common for a CDW transition^{7,9–14,23} which is often second order and usually manifests an increase in resistivity due to a reduction of the density of states at the Fermi energy due to opening up of a gap in the electronic density of states at the Fermi surface. We did not observe T^2 behavior of the resistivity down to our base temperature.

Figure. 7 shows the temperature dependence of the magnetic susceptibility $\chi(T)$. Since the signal from one piece of single crystal is very low and in order to measure the magnetic susceptibility, we measured the magnetization of several single crystals encapsulated in a sample holder and subtract the background signal due to the sample holder. The negative value of the magnetic

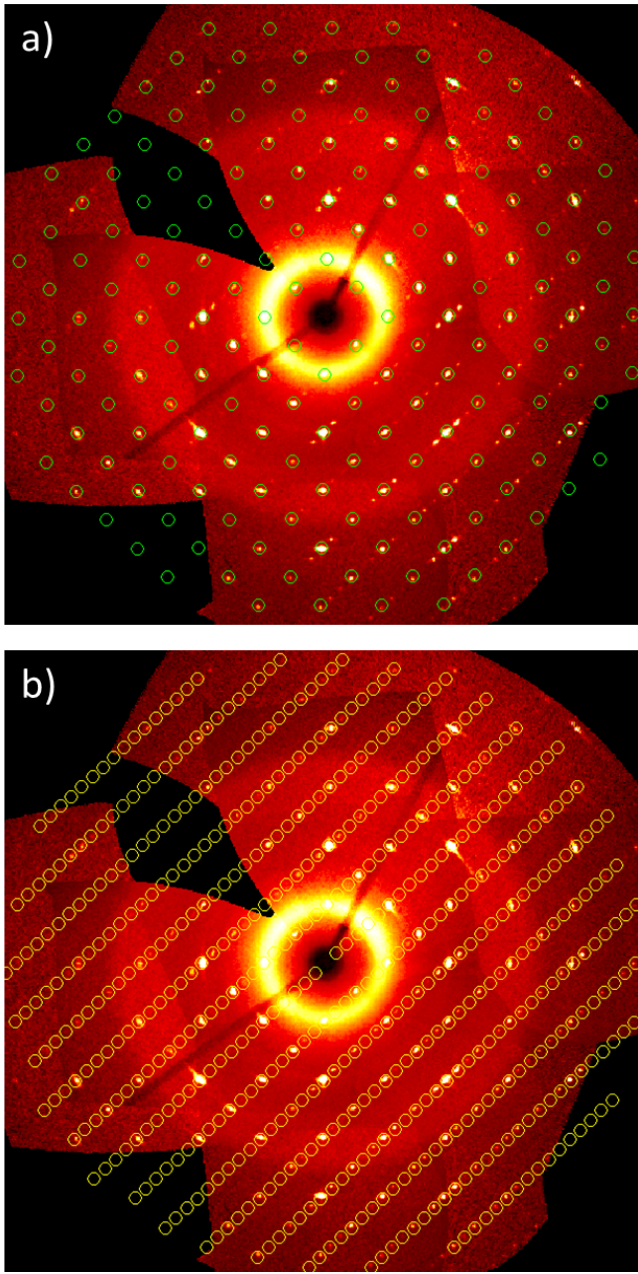


FIG. 2. Precession images of (h 0 l) zone of a $\text{Bi}_2\text{Rh}_3\text{S}_2$ single crystal at 120 K. Green circles in (a) denote reflections that can be indexed by the base cell ($C2/m$, $a = 11.291(3) \text{ \AA}$, $b = 8.378(2) \text{ \AA}$, $c = 7.942(2) \text{ \AA}$, $\beta = 133.286(2)^\circ$), note that many reflections can not be indexed. Yellow circles in (b) denote the reflections that can be indexed by the supercell ($a = 11.542(2) \text{ \AA}$, $b = 8.341(2) \text{ \AA}$, $c = 17.768(4) \text{ \AA}$, $\beta = 107.614(2)^\circ$)

susceptibility indicates the overall diamagnetic behavior of this compound. This is due to the dominating contribution from core diamagnetism. By subtracting the core diamagnetic contribution^{37,38} we can estimate the electronic contribution to the susceptibility. The inset of

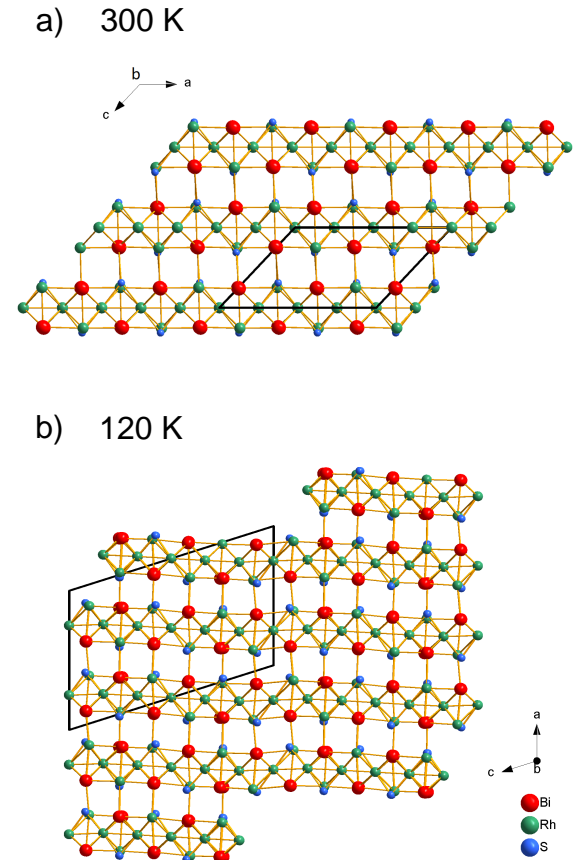


FIG. 3. Crystal structure of $\text{Bi}_2\text{Rh}_3\text{S}_2$ at 300 K (a) and 120 K (b). The black line represents the unit cell.

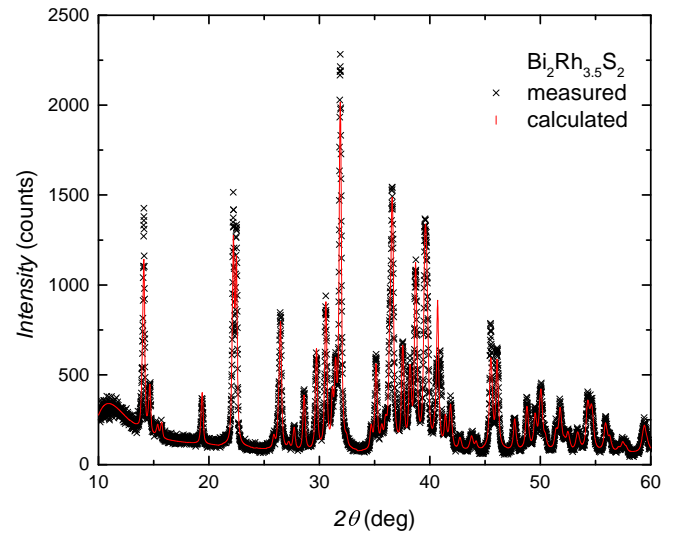


FIG. 4. Powder diffraction pattern of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$. The red line represents the calculated diffraction pattern

Fig.7 shows the temperature dependence of the electronic

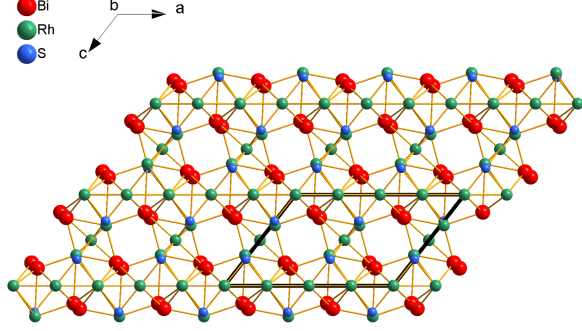


FIG. 5. Crystal structure of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$. The black line represents the unit cell.

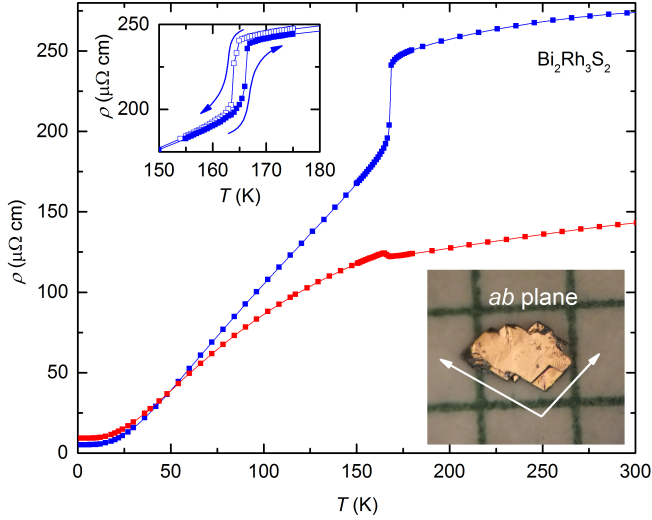


FIG. 6. Temperature dependence of resistivity of the phase pure $\text{Bi}_2\text{Rh}_3\text{S}_2$. The upper inset shows thermal hysteresis observed at 165 K in resistivity measurement. The lower inset shows a picture of the single crystal of $\text{Bi}_2\text{Rh}_3\text{S}_2$ on a millimeter grid. Resistivity data were measured on two different samples with current along the directions of white color arrows

contribution to the magnetic susceptibility, after the diamagnetic correction^{37,38} ($\chi_{\text{core}} = -17 \times 10^{-5} \text{ emu mol}^{-1}$). Susceptibility linearly decreases with the decreasing temperature down to 165 K and then shows dramatic change at 165 K. Given that both Pauli paramagnetic and Landau diamagnetic susceptibility are proportional to the density of state at the Fermi level $D(\epsilon_F)$, the change in χ at 165 K is consistent with an increase in the density of state at the Fermi level $D(\epsilon_F)$. In a typical CDW material there is a reduction of the density of state at the Fermi energy due to opening up of a gap in the electronic

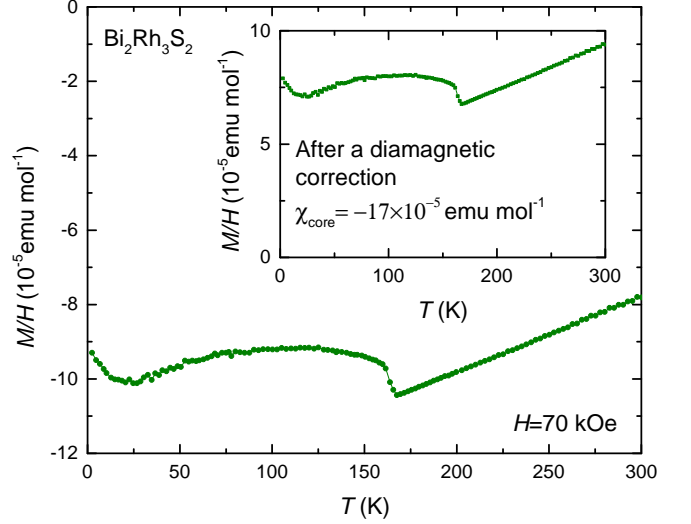


FIG. 7. Temperature dependence of susceptibility of phase pure $\text{Bi}_2\text{Rh}_3\text{S}_2$ before diamagnetic correction ($\chi_{\text{core}} = -17 \times 10^{-5} \text{ emu mol}^{-1}$)^{37,38}. The inset shows after diamagnetic correction.

density of states at the Fermi surface. An increase in density of state is not consistent with the CDW mechanism for structural phase transition. The low temperature upturn (below 25 K) in the susceptibility is probably due to the presence of a small amount of paramagnetic impurities in the sample.

The temperature dependent specific heat of $\text{Bi}_2\text{Rh}_3\text{S}_2$ (Fig. 8) shows a broadened latent heat feature, consistent with the first-order like features seen in the resistivity and magnetization data shown in the Figs. 6 and 7. The room temperature specific heat of $\text{Bi}_2\text{Rh}_3\text{S}_2$, $172.6 \text{ J mol}^{-1} \text{ K}^{-1}$, is close to the DulongPetit limit, $C_V = 3nR = 174.6 \text{ J mol}^{-1} \text{ K}^{-1}$. The Sommerfeld coefficient, $\gamma = 9.41 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\beta = 1.49 \text{ mJ mol}^{-1} \text{ K}^{-4}$ values were obtained for the LT phase from the low temperature data fitted with $C_p/T = \gamma + \beta T^2$ as shown in the lower inset of Fig. 8. From β we obtained a Debye temperature (Θ_D) of 209 K by using equation 1 and slightly larger than the value of $\text{Bi}_2\text{Rh}_3\text{S}_2$. This reflects a higher phonon density of states at low energies which are likely due to the presence of the lighter element "Sulfur" compared to "Selenium". A similar value of $\gamma = 9.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$ was obtained in isostructural $\text{Bi}_2\text{Rh}_3\text{Se}_2$ compound²³.

$$\Theta_D = \left(\frac{12\pi^2 n R}{5\beta} \right)^{1/3} \quad (1)$$

With our measurements of single crystal diffraction, resistivity, magnetization and the specific heat, we can conclude the phase transition in $\text{Bi}_2\text{Rh}_3\text{S}_2$ at 165 K is a first order structural phase transition. We do not have clear evidence of a CDW being associated with this transition.

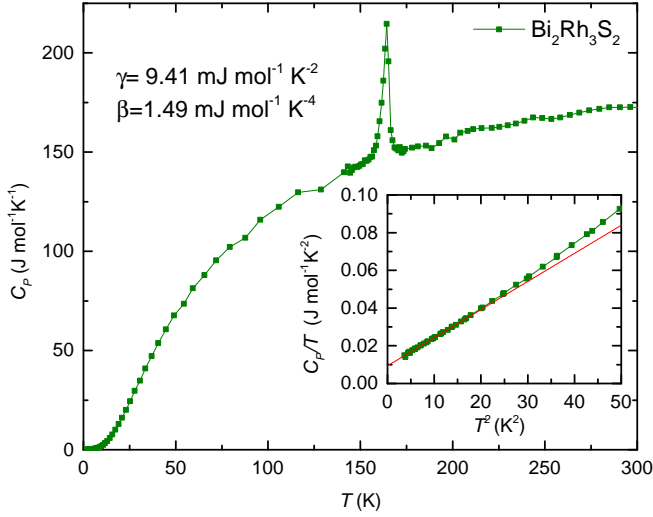


FIG. 8. Temperature dependence of specific heat of phase pure $\text{Bi}_2\text{Rh}_3\text{S}_2$. The lower inset represents the C_p/T vs T^2 graph which used to obtain γ and β values

In the case of $\text{Bi}_2\text{Rh}_3\text{Se}_2$, based on the results of the resistivity, magnetization, thermoelectric power, thermal expansion and low temperature x-ray measurements, Sakamoto et al²³ conclude that the anomaly at ~ 250 K is a CDW transition. However, Chen et al²⁴ report that, based on their experiments of pressure and selected-area electron diffraction study, phase transition at ~ 250 K is not a CDW transition, rather structural transition. In the present case of $\text{Bi}_2\text{Rh}_3\text{S}_2$ further, advanced measurements would be needed to find any support for a possible CDW.

C. Physical properties of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$

Figure 9 presents the temperature dependence of resistivity of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$, which, unlike $\text{Bi}_2\text{Rh}_3\text{S}_2$, does not show any transitions in the resistivity data around 165 K. However, it does manifest zero resistivity below 2 K, indicating an onset of a superconducting transition at this temperature. RRR of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ is 6.4, less than the RRR of $\text{Bi}_2\text{Rh}_3\text{S}_2$. We did not observe T^2 behavior in resistivity down to the base temperature of our measurement.

Figure 10 shows the low temperature specific heat data of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$. The open red squares represent zero field measurements whereas the open black circles represent measurements under 1 T magnetic field, i.e. $H \geq H_{c2}(T)$ for the measured temperature range (see below). From the low temperature data fitted with $C_p/T = \gamma + \beta T^2$ from 2 K to 3.8 K as shown in the upper inset of Fig. 10 we find $\gamma = 22 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and $\beta = 1.94 \text{ mJ mol}^{-1} \text{ K}^{-4}$ and can infer that $\Theta_D = 196$ K. We can clearly see that γ of the superconducting $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ is twice as large as that for the non-superconducting $\text{Bi}_2\text{Rh}_3\text{S}_2$ or $\text{Bi}_2\text{Rh}_3\text{Se}_2$ ²³. Also this value is larger than the other

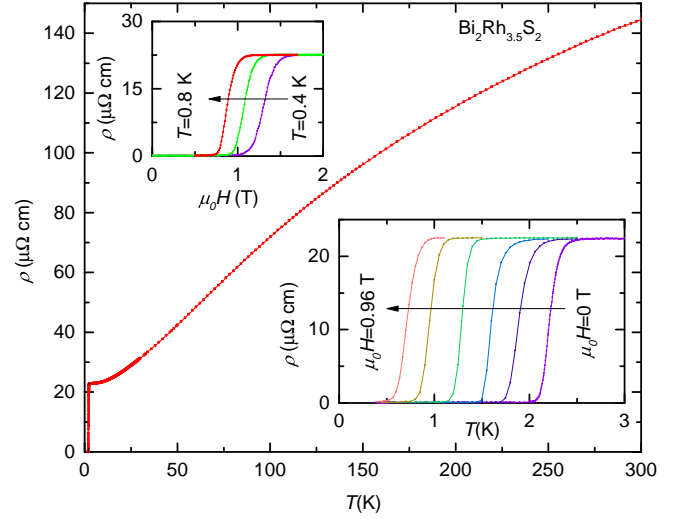


FIG. 9. Temperature dependence of resistivity of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$. Upper inset shows representative field scans of the resistivity at constant temperatures at 0.4 K, 0.6 K and 0.8 K. Lower inset shows representative temperature scans of the resistivity at constant fields at 0 T, 0.08 T, 0.18 T, 0.42 T, 0.74 T and 0.96 T.

reported parkerite-type superconductors, $\text{Bi}_2\text{Ni}_3\text{S}_2$ ²⁰, $\text{Bi}_2\text{Ni}_3\text{Se}_2$ ²⁰ and $\text{Bi}_2\text{Pd}_3\text{Se}_2$ ²¹.

On one hand, $T_c = 1.7$ K was obtained by using an equal entropy construction to the low temperature specific heat data. On the other hand, the $H = 0$ $C_p(T)$ data start to separate from the $H = 1$ T $C_p(T)$ data below 2.2 K. Specific heat jump of $\Delta C = 52.4 \text{ mJ mol}^{-1} \text{ K}^{-1}$ gives $\Delta C/\gamma T_c = 1.39$ which is close to the BCS value 1.43 for a weak-coupling superconductor. The green colored solid line represents a BCS^{4,39} calculation. The deviation above 4 K, normal-state data from the simple Debye model indicates the presence of at least a T^5 term in the lattice contribution.

The lower inset of Fig. 10 shows ZFC data of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$. We were not able to see the full transition in low temperature zero field cooled (ZFC) measurements because the minimum temperature which we can reach in the MPMS is 1.8 K. These data are consistent with the broadened transition seen in the resistivity and the $C_p(T)$ data.

The upper inset of Fig. 9 shows the field dependence of the superconducting transition for temperatures from 0.4 K to 0.8 K and the lower inset shows the temperature dependence of the superconducting transition from 0 T to 0.96 T applied field. Figure 11 shows $\mu_0 H_{c2}(T)$ as a function of the critical temperature determined from the resistivity data. Lower and upper insets show the maximum slope of the resistivity extrapolated to $\rho = 0$, used as a criteria to obtain the $\mu_0 H_{c2}$ and T_c respectively. We can estimate the Ginzburg-Landau (GL) coherence length³⁹ at zero temperature, $\xi(0) = 150 \text{ \AA}$ by using the relation $\mu_0 H_{c2}(0) = \Phi_0/2\pi\xi(0)^2$, in which Φ_0 is the quantum flux and estimating $\mu_0 H_{c2}(0)$ to be 1.5 T. The value

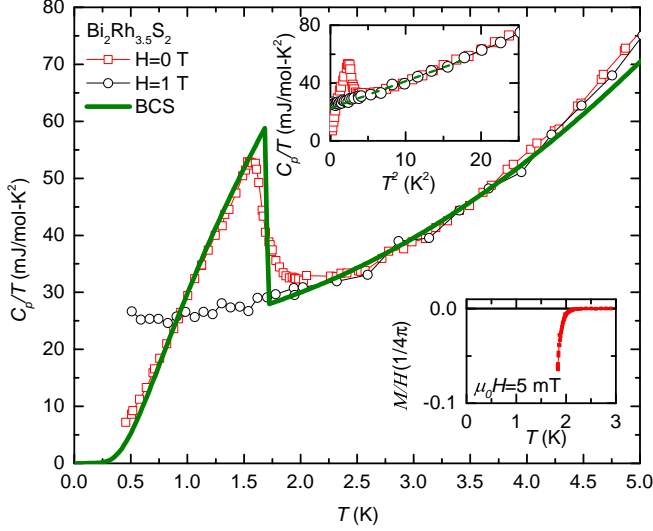


FIG. 10. Low temperature C_p/T vs T of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$. Red open squares represent zero field measurements while black open circles represent measurements under 1 T field. Green color solid line shows the BCS calculation. The upper inset represents the C_p/T vs T^2 graph which used to obtain γ and β values. Lower inset shows ZFC M/H data of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$.

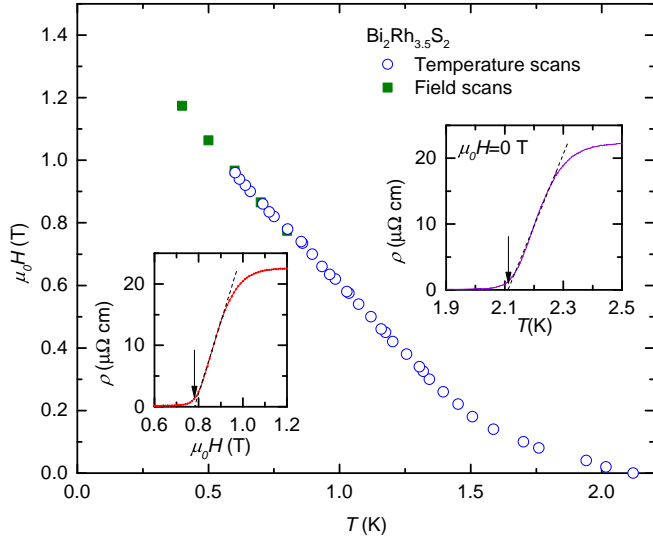


FIG. 11. Temperature dependence of the upper critical field for $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ determined from the resistivity data. Lower and upper insets show the criteria (maximum slope extrapolated to $\rho = 0$) which was used to obtain the data points.

of $\mu_0 H_{c2}(0)$ is well below the Pauli paramagnetic limit⁴⁰ of $\mu_0 H_{c2}^p(0) = 1.85 T_c = 3.15 \text{ T}$, suggesting an orbital pair-breaking mechanism. The upward curvature near T_c in the $H_{c2}(T)$ data shown in Fig. 11 may come from a distribution of T_c values in the sample^{41–44} or multi-band superconductivity as was discussed by Shulga et al⁴⁵ or nonlocal correction^{46,47} to the Ginzburg-Landau equations. Similar $H_{c2}(T)$ curvatures were found for $\text{YNi}_2\text{B}_2\text{C}$ as well as $\text{LuNi}_2\text{B}_2\text{C}$ ⁴⁵.

The electron-phonon coupling constant λ_{e-ph} can be estimated from the McMillan equation⁴⁸ for the superconducting transition temperature (equation 2), for phonon mediated superconductors,

$$T_c = \frac{\Theta_D}{1.45} \exp \left[-\frac{1.04(1 + \lambda_{e-ph})}{\lambda_{e-ph} - \mu^*(1 + 0.62\lambda_{e-ph})} \right] \quad (2)$$

where μ^* , the Coulomb pseudopotential, having value often between 0.1 and 0.2 and usually taken as 0.13⁴⁸. Similar values of μ^* have been used in isostructural compounds^{20,21,23}. Using $\Theta_D = 196 \text{ K}$ and $T_c = 1.7 \text{ K}$ we estimated $\lambda_{e-ph} = 0.54$. A difference of μ from the assumed value of 0.13 will give a different value of λ_{e-ph} . For example, $\lambda_{e-ph} = 0.48$ if $\mu = 0.1$ and $\lambda_{e-ph} = 0.69$ if $\mu = 0.2$. By using both normal state and superconducting state specific heat data, one can obtain the thermodynamic critical field, $\mu_0 H_c(0)$ as a function of temperature from equation 3

$$\frac{\mu_0 V_m H_c(0)^2}{2} = \int_0^{T_c} \Delta S(T') dT' \quad (3)$$

in which $\Delta S(T)$ is the entropy difference between the normal and superconducting states and V_m ($8.54 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$) is the molar volume. The calculated value of $\mu_0 H_c(0)$ is 23 mT for $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$. This value is larger than the value of $\text{Bi}_2\text{Rh}_3\text{Se}_2$ and clearly reflects the larger γ and T_c of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$.

$$\mu_0 H_c(0) = 1.76 \times 10^{-4} (4\pi D(\epsilon_F))^{1/2} k_B T_c \quad (4a)$$

$$\frac{\gamma}{V_m} = \frac{1}{15} \pi^2 D(\epsilon_F) k_B^2 \quad (4b)$$

$$\mu_0 H_c(0) = 1.76 \left(\frac{6\gamma\mu_0}{4\pi^2 V_m} \right)^{1/2} T_c \quad (4c)$$

Using BCS theory results⁴ (equation 4a and 4b) we can eliminate the $D(\epsilon_F)$ term and, for the limit of an isotropic gap function, use equation 4c to calculate the value of $\mu_0 H_c(0) = 21 \text{ mT}$. This value is close to the calculated value using specific heat.

Also the penetration depth $\lambda(0)$ and GL parameter κ are found to be 7450 \AA and 50 from equations 5 and 6, respectively.

$$\mu_0 H_c(0) \approx \frac{\Phi_0}{2\sqrt{2}\lambda(0)\xi(0)} \quad (5)$$

$$\kappa \approx \frac{\lambda(0)}{\xi(0)} \quad (6)$$

From the specific heat jump and using Rutgers's relation, $\Delta C/T_c = (1/8\pi\kappa^2)(dH_{c2}/dT)|_{T_c}$ ⁴⁹, one can obtain a similar κ value of 30. The obtained $\lambda(0)$ and κ values of $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ are smaller than the values of $\text{Bi}_2\text{Rh}_3\text{Se}_2$ ²³ but the value of κ ($\kappa > 1/\sqrt{2}$) is large enough to consider $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ is a type II superconductor.

IV. CONCLUSIONS

Single crystals of the closely related $\text{Bi}_2\text{Rh}_3\text{S}_2$ and $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ systems were synthesized by high temperature solution growth. Resistivity, magnetization, and specific heat measurements were carried out to characterize their normal states and, for $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$, superconducting properties. $\text{Bi}_2\text{Rh}_3\text{S}_2$ manifests a structural phase transition around 165 K. No superconductivity was observed down to 0.5 K. Single crystal diffraction measurements at 120 K and 300 K confirmed that a 3-fold superstructure develops. We noticed a large, in-plane, resistivity anisotropy in this compound. Thermal hysteresis and the specific heat feature at 165 K are consistent with a first-order phase transition. The Sommerfeld coefficient $\gamma = 9.41 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and the Debye temperature $= 209 \text{ K}$ were calculated by using low temperature specific heat data. Based on our measurements, we do not have evidence of a CDW type mechanism being responsible for this transition.

$\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ adopts a monoclinic (C/2m) crystal structure. This material shows a signature of superconductivity in the resistivity and specific heat measurements consistent with bulk superconductivity below the critical temperature T_c of 1.7 K. The calculated values for the Sommerfeld coefficient and the Debye temperature are $22 \text{ mJ mol}^{-1} \text{ K}^{-2}$ and 196 K respectively. Analysis of the jump in the specific heat at T_c , suggest that $\text{Bi}_2\text{Rh}_{3.5}\text{S}_2$ as a weak electron-phonon coupled, BCS superconductor.

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- ¹ R. Peierls, *Annalen der Physik* **396**, 121 (1930).
- ² R. E. Peierls, *Quantum theory of solids* (Clarendon, Oxford, 1955).
- ³ H. Fröhlich, *P. Roy. Soc. A-Math. Phys* **223**, pp. 296 (1954).
- ⁴ J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).
- ⁵ A. M. Gabovich and A. I. Voitenko, *Low. Temp. Phys* **26**, 305 (2000).
- ⁶ A. M. Gabovich, A. I. Voitenko, J. F. Annett, and M. Ausloos, *Supercond. Sci. Tech* **14**, R1 (2001).
- ⁷ J. A. Wilson, F. J. Di Salvo, and S. Mahajan, *Phys. Rev. Lett.* **32**, 882 (1974).
- ⁸ J. Harper, T. Geballe, and F. D. Salvo, *Phys. Lett A* **54**, 27 (1975).
- ⁹ P. Monceau, N. P. Ong, A. M. Portis, A. Meerschaut, and J. Rouxel, *Phys. Rev. Lett.* **37**, 602 (1976).
- ¹⁰ F. J. Di Salvo, D. E. Moncton, and J. V. Waszczak, *Phys. Rev. B* **14**, 4321 (1976).
- ¹¹ R. N. Shelton, L. S. Hausermann-Berg, P. Klavins, H. D. Yang, M. S. Anderson, and C. A. Swenson, *Phys. Rev. B* **34**, 4590 (1986).
- ¹² B. Becker, N. G. Patil, S. Ramakrishnan, A. A. Menovsky, G. J. Nieuwenhuys, J. A. Mydosh, M. Kohgi, and K. Iwasa, *Phys. Rev. B* **59**, 7266 (1999).
- ¹³ S. Ramakrishnan, *Pramana* **58**, 827 (2002).
- ¹⁴ Y. Singh, D. Pal, S. Ramakrishnan, A. M. Awasthi, and S. K. Malik, *Phys. Rev. B* **71**, 045109 (2005).
- ¹⁵ E. Morosan, H. W. Zandbergen, B. S. Dennis, J. W. G. Bos, Y. Onose, T. Klimczuk, A. P. Ramirez, N. P. Ong, and R. J. Cava, *Nat Phys* **2**, 544 (2006).
- ¹⁶ C. Michener and M. Peacock, *Am. Mineral* **28**, 343 (1943).
- ¹⁷ M. Peacock and J. McAndrew, *Am. Mineral* **35**, 425 (1950).
- ¹⁸ W. Brower, H. Parker, and R. Roth, *Am. Mineral* **59**, 296 (1974).
- ¹⁹ S. Natarajan, G. Rao, R. Baskaran, and T. Radhakrishnan, *J. Less-Common. Met* **138**, 215 (1988).
- ²⁰ T. Sakamoto, M. Wakeshima, and Y. Hinatsu, *J Phys-Condens. Mat* **18**, 4417 (2006).
- ²¹ T. Sakamoto, M. Wakeshima, Y. Hinatsu, and K. Matsuhira, *Phys. Rev. B* **78**, 024509 (2008).
- ²² X. Lin, S. L. Bud'ko, and P. C. Canfield, *Philos. Mag* **92**, 2436 (2012).
- ²³ T. Sakamoto, M. Wakeshima, Y. Hinatsu, and K. Matsuhira, *Phys. Rev. B* **75**, 060503 (2007).
- ²⁴ C. Chen, C. Chan, S. Mukherjee, C. Chou, C. Tseng, S. Hsu, M.-W. Chu, J.-Y. Lin, and H. Yang, *Solid. State. Commun* **177**, 42 (2014).
- ²⁵ C. W. Chu, V. Diatschenko, C. Y. Huang, and F. J. DiSalvo, *Phys. Rev. B* **15**, 1340 (1977).
- ²⁶ A. Briggs, P. Monceau, M. Nunez-Regueiro, J. Peyrard, M. Ribault, and J. Richard, *J. Phys. C. Solid. State* **13**, 2117 (1980).
- ²⁷ S. L. Bud'ko, T. A. Wiener, R. A. Ribeiro, P. C. Canfield, Y. Lee, T. Vogt, and A. H. Lacerda, *Phys. Rev. B* **73**, 184111 (2006).
- ²⁸ P. C. Canfield and Z. Fisk, *Philos. Mag. B* **65**, 1117 (1992).
- ²⁹ P. C. Canfield and I. R. Fisher, *Journal of Crystal Growth* **225**, 155 (2001).
- ³⁰ C. Petrovic, P. C. Canfield, and J. Y. Mellen, *Philos. Mag.* **92**, 2448 (2012).
- ³¹ B. H. Toby, *Journal of Applied Crystallography* **34**, 210 (2001).
- ³² A. Larson and R. Von Dreele, *General Structure Analysis (GSAS)*, Los Alamos National Laboratory, report laur 86-748 ed. (2000.).
- ³³ *SMART version 5*, Bruker AXS, Madison WI., smart version 5 ed. (2003).
- ³⁴ R. H. Blessing, *Acta. Crystallogr. A* **51**, 33 (1995).
- ³⁵ G. Sheldrick, Bruker AXS, Madison, WI, shelx, version 5.1 ed. (2002).
- ³⁶ I. Anusca, A. Schmid, P. Peter, J. Rothballer, F. Pielhofer, and R. Weihrich, *Z. Anorg. Allg. Chem.* **635**, 2410 (2009).
- ³⁷ E.A. Boudreaux and L.N. Mulay, *Theory and Applications of Molecular Paramagnetism* (John Wiley and Sons, New York, 1976).
- ³⁸ G. A. Bain and J. F. Berry, *J. Chem. Educ* **85**, 532 (2008).
- ³⁹ M. Tinkham, *Introduction to Superconductivity (2nd Edition)* (Dover Publications, New York, 1996).
- ⁴⁰ A. M. Clogston, *Phys. Rev. Lett.* **9**, 266 (1962).
- ⁴¹ T. Park, E. Park, H. Lee, T. Klimczuk, E. D. Bauer, F. Ronning, and J. D. Thompson, *J Phys-Condens. Mat* **20**, 322204 (2008).
- ⁴² H. Xiao, T. Hu, A. P. Dioguardi, N. apRoberts-Warren, A. C. Shockley, J. Crocker, D. M. Nisson, Z. Viskadourakis, X. Tee, I. Radulov, C. C. Almasan, N. J. Curro, and C. Panagopoulos, *Phys. Rev. B* **85**, 024530 (2012).
- ⁴³ H. Xiao, T. Hu, S. K. He, B. Shen, W. J. Zhang, B. Xu, K. F. He, J. Han, Y. P. Singh, H. H. Wen, X. G. Qiu, C. Panagopoulos, and C. C. Almasan, *Phys. Rev. B* **86**, 064521 (2012).
- ⁴⁴ A. Ślebarski, M. Fijałkowski, M. M. Maška, M. Mierzejewski, B. D. White, and M. B. Maple, *Phys. Rev. B* **89**, 125111 (2014).
- ⁴⁵ S. V. Shulga, S.-L. Drechsler, G. Fuchs, K.-H. Müller, K. Winzer, M. Heinecke, and K. Krug, *Phys. Rev. Lett.* **80**, 1730 (1998).
- ⁴⁶ P. C. Hohenberg and N. R. Werthamer, *Phys. Rev.* **153**, 493 (1967).
- ⁴⁷ V. Metlushko, U. Welp, A. Koshelev, I. Aranson, G. W. Crabtree, and P. C. Canfield, *Phys. Rev. Lett.* **79**, 1738 (1997).
- ⁴⁸ W. L. McMillan, *Phys. Rev.* **167**, 331 (1968).
- ⁴⁹ U. Welp, W. K. Kwok, G. W. Crabtree, K. G. Vandervoort, and J. Z. Liu, *Phys. Rev. Lett.* **62**, 1908 (1989).